

DIFFUSION IN THE LIQUID-VAPOR CRITICAL REGION

L. A. Rott

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 1.00Microfiche (MF) 50

ff 653 July 65

Translation of "Diffuziya v kriticheskoy oblasti zhidkost'-par."
Inzhenerno-Fizicheskiy Zhurnal,
Vol. 7, No. 3, pp. 78-81, 1964.

N65-29734

(ACCESSION NUMBER)	(THRU)
<u>8</u>	<u>1</u>
(PAGES)	(CODE)
(NASA CR OR TMX OR AD NUMBER)	<u>12</u>
	(CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON JULY 1965

DIFFUSION IN THE LIQUID-VAPOR CRITICAL REGION

78*

ABSTRACT

29734

The equation of isothermal convective molecular diffusion in a binary gaseous mixture is investigated in the liquid-vapor critical region. This phenomenon is accompanied by convective motion of the mixture. As in the critical layerwise separation of a binary liquid system, isothermal diffusion is instigated by the chemical potential gradient of one of the components. The investigated equation can be reduced to the ordinary Fick diffusion equation. Toward this end, it is necessary also to define a function to be interpreted as the diffusion coefficient in the critical region. The diffusion coefficient is shown to have both positive and negative values.

The peculiarities of diffusion in the critical region of binary gaseous mixture first came under critical scrutiny in reference 1. This is a phenomenon of appreciable practical and theoretical interest.

It is evident in the experimental curve of the "molar volume of the homogeneous solution (v) versus the molar fraction of one component (N_2)" that the vicinity of the critical point is where significant changes in volume occur. There is little doubt, then, that an intensive variation in molar volume with varying composition must give rise to convection motion of the mixture as a whole.

*Numbers in the margin indicate pagination in the original foreign text.

For a liquid system, the assumptions are valid that the partial molar volumes \bar{v}_1 and \bar{v}_2 in the region of critical concentration depend only very slightly on the composition of the solution, and that $N_2(\bar{v}_2 - \bar{v}_1)/v \ll 1$, the condition stipulated in reference 2 in connection with the diffusion of a critical liquid phase in the layer separation region. In the case of a gaseous mixture, on the other hand, such assumptions plainly do not exist.

Attempts to apply the ordinary diffusion equation of Fick to the interpretation of the experimental data necessitate the supposition that the diffusion coefficient can take on positive as well as negative values, which, taken by itself, appears paradoxical. The inapplicability of the Fick equation in the critical region of separation is patent (ref. 3). The same must also be true of a binary system in the critical liquid-vapor region, since the thermodynamic criterion of the latter is the same as for the region of separation (ref. 4).

The equation of isothermal convective molecular diffusion, taking into account the compressibility of the mixture, is written in the form

$$\frac{\partial c}{\partial t} + \text{div}(\bar{c}\bar{u}) = -\frac{D_0}{RT} \text{div}(c \text{ grad } \mu), \quad (1)$$

where $c = N/v$ (to simplify the writing, the component subscript is dropped), $D_0 = \text{const.}$

Equation (1) differs from the diffusion equation for a binary liquid system by the presence of the term $\text{div}(\bar{c}\bar{u})$, which accounts for convective diffusion (ref. 5).

The following conditions must be satisfied at the critical point:

$$\frac{\partial \mu}{\partial N} = 0; \quad \frac{\partial^2 \mu}{\partial N^2} = 0. \quad (2)$$

The fact that the derivative of the chemical potential with respect to the molar fraction goes to zero also indicates the cessation of diffusion at the

critical point. The criterion (2) implies that first- and second-order terms do not appear in the series expansion of the chemical potential with respect to $N - N_k$. Retaining the first two terms of the expansion, we can write

$$\mu = \text{const} + \beta (N - N_k)^2. \quad (3)$$

With the expansion (3), equation (1) is conveniently rewritten in terms of the molar fraction N . We will then proceed from the fact that the pressure throughout the entire system may be considered constant, i.e., $dP/dt = 0$. And since $P = P(N, v)$, an expression can be found for the velocity of the mixture $u = (\partial v / \partial t)_N$ (treating the one-dimensional case of motion along a capillary of unit cross section):

$$u = - \left(\frac{\partial P}{\partial N} \right)_v \left(\frac{\partial N}{\partial t} \right)_v \bigg/ \left(\frac{\partial P}{\partial v} \right)_N. \quad (4)$$

The analysis corresponds to division of the convective diffusion process into two stages; we assume that at first in the elementary volume the molar composition changes, then at constant composition the volume changes until pressure equilibrium is established.

The limiting solution ($N \rightarrow N_k$) of the isothermal diffusion equation in the absence of convection has the following form in the one-dimensional case (ref. 2):

$$N = N_k \exp \left\{ \left(\sqrt{\frac{b_1}{A}} x + b_2 \right) / (2(-b_1 t + 1))^{\frac{1}{2}} \right\} A, b_1, b_2 = \text{const.} \quad (5)$$

The different values of x correspond to different values of the molar volume.

We say, therefore, that a fixed value of v corresponds to a fixed value of x .

From the solution (5) we obtain an expression for $(\partial N / \partial t)_v$, from which it is

apparent that for $N = N_k$ we will have $u = 0$, i.e., when diffusion ceases at the

critical point, the mixture will cease to move (we note that $(\partial P / \partial v)_{N_k} \neq 0$).

Within a small interval of the molar fraction about its critical value, we can make use of the expansion

$$P = P_0 + P_1(N - N_k), \quad (6)$$

whereupon it is valid to assume that the ratio

$$\left(\frac{\partial P}{\partial N} \right)_v / \left(\frac{\partial P}{\partial v} \right)_N \approx P_1 \left(\frac{\partial P_0}{\partial v} \right)_N^{-1} \quad (7)$$

is constant.

Making use of the transformation $\phi = \ln(N/N_k)$, we obtain an approximate expression for the velocity of the mixture:

$$u = - \frac{AP_1 N_k}{(\partial P_0 / \partial v)_N} \varphi \left(\frac{\partial \varphi}{\partial x} \right)^2 \quad (8)$$

Let us substitute the expansion (3) and equation (8) into (1). We replace the terms $\frac{N}{v} \partial v / \partial N$ by their mean values. This is equivalent to linearizing the dependence of the volume on the molar fraction in the vicinity of the critical point, which is not inconsistent with the experimental data in the given approximation. Neglecting terms containing second and higher powers of ϕ , we obtain an approximate equation for the isothermal convective diffusion in the critical region. In the one-dimensional case, it has the form

$$\begin{aligned} \frac{\partial \varphi}{\partial t} + D_1 \varphi \frac{\partial \varphi}{\partial x} \frac{\partial^2 \varphi}{\partial x^2} + D_2 \left(\frac{\partial \varphi}{\partial x} \right)^3 + D_3 \varphi \left(\frac{\partial \varphi}{\partial x} \right)^2 &= 0, \\ \text{where} \quad D_1 = 2D_2; \quad D_2 = AP_1 N_k \left[\left(\frac{\partial P_0}{\partial v} \right)_N \left(1 - \frac{N}{v} \frac{\partial v}{\partial N} \right) \right]^{-1}. \end{aligned} \quad (9)$$

Equation (9) permits separation of the variables $\phi = y(x)\theta(t)$. In the y-part of the equation we perform the substitution $dy/dx = k_1/z(y)$;

$k_1 = \sqrt{\lambda/D_3}$. With respect to z, we obtain the equation

$$z' - \frac{1}{2y} z + k(z^2 - z^4) = 0, \quad k = -D_3^{1/2} (\lambda^{1/2} D_1)^{-1}. \quad (10)$$

For the given problem, we are interested in the case when $|z| \gg 1$. Then the final solution of equation (9) reduces to quadratures.

The diffusion equation (9) can be transformed to the ordinary Fick equation

$$\frac{\partial c}{\partial t} + \frac{\partial (cu)}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right), \quad (11)$$

but, in so doing, it is necessary to determine the function $D(N)$ that we will interpret as the diffusion coefficient in the critical region (an analogous diffusion coefficient was defined for a liquid system in the critical separation region).

In D, we obtain the equation

$$\frac{\partial D}{\partial x} + \psi(x, t) D + f(x, t) = 0,$$

where

$$\psi = L \theta(t) y'(x) + \frac{y''(x)}{y'(x)};$$

$$f(x, t) = \frac{AP_1 N_K}{(\partial P_0 / \partial v)_{N_K}} \theta'' y' (yy'' + y'^2 + 2yy''') - \frac{N}{v} \left(1 - \frac{N}{v} \frac{\partial v}{\partial N} \right) \theta' y; \quad (12)$$

$$L = \left(1 - 3 \frac{N}{v} \frac{\partial v}{\partial N} + 2 \left(\frac{N}{v} \frac{\partial v}{\partial N} \right)^2 - \frac{N^2}{v} \frac{\partial^2 v}{\partial N^2} \right) \left(1 - \frac{N}{v} \frac{\partial v}{\partial N} \right)^{-1}.$$

It follows from estimates based on the data of reference 1 that L does not have any singularities and its absolute value is much smaller than unity (which

means that the exponential factor in the integrands, $\exp(\int \psi dx)$ can be replaced by a linear expression).

Since the sought-after function $N(x, t)$ has the form

$$N = N_k \exp \left[\left(\frac{16\lambda_1}{45D_1} \right)^{\frac{1}{2}} x^{\frac{1}{2}} (2\lambda_2 t + 1)^{-\frac{1}{2}} \right], \quad \lambda_1, \lambda_2 = \text{const}, \quad (13)$$

for the function D we obtain the expression

$$D = B_1(t) \left(\ln \frac{N}{N_k} \right)^{\frac{1}{2}} + B_2(t) \left(\ln \frac{N}{N_k} \right)^{\frac{1}{2}} + B_3(t) \left(\ln \frac{N}{N_k} \right)^{\frac{1}{2}}. \quad (14)$$

It is apparent from the solution (14) that for $N = N_k$ the diffusion coefficient goes to zero (as $t \rightarrow \infty$ $B_1, B_2, B_3 \rightarrow 0$). In the vicinity of the critical point, i.e., as $N \rightarrow N_k$, we can write

$$D \sim \left(\ln \frac{N}{N_k} \right)^{\frac{1}{3}}.$$

Hence it is clear that the diffusion coefficient can take on either positive or negative values. In the vicinity of the critical point for layer separation of a liquid system (in the absence of convective motion of the mixture), the diffusion coefficient assumes only positive values and at the critical point itself has a minimum equal to zero (ref. 2).

NOTATION

v is the molar volume of the homogeneous solution, N the molar fraction of a given component of the mixture, \bar{v} the partial molar volume of the component, c the volume concentration, μ the chemical potential of the component, T the temperature, R the gas constant, u the velocity of the mixture, P the pressure, D the diffusion coefficient. The subscript "k" refers to the critical state, an overhead bar denotes averaging.

REFERENCES

1. Krichevskiy, I. R., Khazanova, N. Ye. and L. S. Lesnevskaya. Inzh. Fiz. Zh., No. 2, 1962.
2. Rott, L. A. Dokl. Akad. Nauk SSSR, Vol. 121, p. 678, 1958.
3. Collection: Critical Phenomena and Fluctuations in Solutions (Kriticheskiye yavleniya i fluktuatsii v rastvorakh). Izd. AN SSSR (Publishing House of the Academy of Sciences of the USSR), 1960.
4. Krichevskii, I. R. Phase Equilibrium in Solutions at High Pressures (Fazovyye ravnovesiya v rastvorakh pri vysokikh davleniyakh). Goskhimizdat, 1952.
5. Leivch, V. G. Physicochemical Hydrodynamics (Fiziko-khimicheskaya gidrodinamika). Fizmatgiz, 1959.

Translated for NASA by Stemar Engineering, Inc.
4940 Long Beach Blvd., Long Beach, California